The new game in NOx reduction

GAS TURBINE OPERATING CONDITIONS ARE TOUGHER NOW BUT CATALYST SYSTEMS ADAPT AND SUCCEED

FLEMING HANSEN AND PETER LINDENHOFF HALDOR TOPSOE

Selective Catalytic Reduction (SCR) systems have successfully reduced NOx emissions from gas turbines for decades. With more stringent emission limits for NOx, SOx, particulate matter and CO, the operating conditions for the SCR catalyst have become more demanding. Catalyst makers have responded by adapting SCR systems to meet performance requirements in these more-demanding conditions.

In recent years many gas turbines have been used as peaking units in simple cycles, and SCRs have had to be applied to meet local air permits. But in simple cycles, the SCR operates at higher temperatures and in a cyclic operation, which can lead to catalyst deactivation.

In some regions, permitting levels for NOx have been reduced to less than 2 ppm. In installations with a CO catalyst upstream of the SCR, high NO2 levels have been observed that, in the worst cases, can lead to less NOx reduction. Moreover, fuel oil is increasingly replacing expensive natural gas. But experience shows that SCRs can be designed to meet current environment criteria for fuel oil.

Improving performance

Today, SCRs are operating under tougher environmental rules. Many of the earlier turbines with SCRs were cogeneration units and combined cycle units with permitted NOx emissions of 5 to 10 ppm with 10 ppm ammonia slip. Lately, permitted levels have come down to 2 ppm NOx and 5 or even 2 ppm NH3 slip.

In catalyst operation, the NH3/NOx ratio has to be close to stochiometric. Therefore ammonia and flue gas should be mixed almost perfectly to

Figure 1: A good distribution of ammonia is needed to have high NOx conversion and low ammonia slip. An increase in RMS values means a decrease in NOx-Ammonia mixing

Figure 2: Experience shows that SCRs in oil-fired turbines can reduce NOx values to below permissible levels. Above is a graph of NOx values from an LM6000 firing oil
Figure 3: Higher operating temperatures do not significantly increase catalyst deactivation rates. $k$ is catalyst activity at a given time and $k_0$ is the activity when the catalyst was new.

Figure 4: Catalysts can be designed to achieve permissible NOx conversion values within a few minutes of turbine ignition. An LM6000 operating in simple cycle mode.

meet the high reduction rates demanded, without exceeding the amount of unreacted ammonia passing through.

Figure 1 illustrates the relationship between NOx conversion and ammonia slip for various levels of homogeneity of the ammonia-NOx mixture — expressed as a root mean square (RMS) value — for a fixed reactor design. Effective mixing is achieved when the ammonia-NOx ratio has less than 5% RMS (0% RMS is perfect mixing). The limit for NOx conversion in this case is about 95%. If the catalyst volume is increased, a higher conversion can be achieved. It is obvious that with a poor distribution of ammonia it is not possible to have high conversion as well as low ammonia slip. So the catalyst volume needs to be higher, not just to handle the higher temperatures but also to reduce slip.

Along with the mixing of ammonia and NOx, turbomachinery users should also pay attention to the design of ammonia injection lances. This is particularly important if the mixture of ammonia and dilution air is injected at a temperature much below that of the flue gas.

Large temperature gradients in the lances that occur as the ammonia mixture is warming up to the temperature of the flue gas can present a design problem due to the thermal expansion of the NH3-air mixture. Unless the changing density of the ammonia-air mixture is taken into account in calculating pressure loss in the nozzles there will be a skewed distribution of ammonia in the duct.

A proper Computational Fluid Dynamics model of the ammonia injection lances is required for the design if the temperature difference between the flue gas and the ammonia-air mixture is more than 200-300 °F.

**Facing the heat**

Catalyst operating lives of 10 or more years used to be common, but in recent years many incidents of shorter-than-expected lifetimes of the SCR catalyst have been reported. Several plants have had to add more catalyst to meet initial performance test criteria, or the catalyst had to be replaced prematurely.

Various reasons have been given for the SCR failures. Recently some simple cycle turbine operators have reported catalyst poisoning by sodium.

Sodium and other alkali metals are poisonous to the SCR catalyst as they bond to the active sites on the catalyst. Sodium can come from the solution of ammonia water that is injected, salty air intake or the fuel itself. But a study of the failed catalysts shows that sodium alone cannot explain the inability to meet performance criteria, and usually there is more than one reason for such failures. Internal catalyst bypasses, poisoning, deviations from the design point in operating conditions, and an inadequate ammonia injection system can alone or together have caused the failures.

Meanwhile, higher catalyst operating temperatures have forced manufacturers to consider modifications in the catalyst composition and equipment. For instance, until a few years ago only zeolite-type catalysts were available for operating temperatures above 800-850°F. However, several catalyst manufacturers have managed to modify the common titania, vanadium and tungsten type to work at temperatures close to 1,000°F and are offering them as alternatives to zeolite-based catalysts.

At higher temperatures, a larger catalyst volume than what is required at 700-800°F would be needed to achieve the same performance. This achieves the necessary thermal stability, mitigates ammonia oxidation and offsets the fact that less ammonia will be adsorbed onto the catalyst at higher temperatures.

Alternatively, fans that supply tempering air in front of the catalyst to cool it to 700-800°F can be used. This will be economical in some cases, especially in peaking plants, where the lower catalyst volume in a less costly steel frame justifies the extra cost of fan power. For a typical
LM6000 the catalyst volume can be lowered by about 30% if the gas is cooled from 875°F to below 800°F. For a large frame machine operating with exhaust at 1,000-1,100°F the savings in catalyst volume can be even larger. If the cooling air blowers are used, their operation should be included in the control system so that large temperature excursions that could weaken the steel frames and injure the catalyst are avoided.

**Firing oil**

With natural gas prices increasing, oil is replacing gas in many turbines. Oil contains small amounts of metals including some that may poison the catalyst such as iron, nickel and alkali metals (sodium and potassium). Sulfur, whether in oil or natural gas, will be oxidized in the combustor to SO₂ and some SO₃. If a CO oxidation catalyst has been installed, a larger fraction of the SO₂ will be oxidized to SO₃ over this catalyst and a smaller fraction of the gas will oxidize over the SCR catalyst.

SOₓ is a potential precursor for particulate matter and should therefore be limited. SO₃ may react with residual ammonia in the stack or preheater section to form ammonium bisulfate (ABS). ABS is a sticky substance that can cause corrosion of the tube bundle and stack and lead to poor heat transfer in the preheater of the heat recovery section. Sulfur will become an irrelevant issue once it becomes mandatory to use Ultra Low Sulfur Diesel.

Vanadium also affects burning oil. Some of the vanadium will be absorbed by the catalyst and this could help offset catalyst deactivation from other sources. However, the metal is active for both the SCR reaction and the oxidation of SO₂ to SO₃. So, as the vanadium composition in the catalyst increases, the SO₂ oxidation level will increase, which may limit catalyst life. [1]

But experience from several turbines firing oil shows that the deactivation was limited to only a few percent per year, and actually in some cases an increase in activity has been seen. For simple cycle turbines with only limited run times, it is difficult to isolate the effect of oil-firing versus other issues such as standstill and thermal cycling. [2]

Oil-fired turbines can be designed for NOₓ conversion rates similar to that of gas operated turbines. For dual-fuel turbines, the outlet NOₓ can be designed to be equal for both the fuels. For turbines with about 40 ppm NOₓ when firing oil, a reduction to less than 5 ppm NOₓ and 2 ppm NH₃ slip is attainable (Figure 2). Oil firing in turbines therefore seems to be manageable from both environmental and operational perspectives.

Data from combined cycle or cogen operating at temperatures 600-750°F show practically no catalyst deactivation over time. For higher temperatures, limited deactivation has been experienced. Figure 3 shows relative activity expressed as k/k₀ for five turbines with more than 100 starts a year.

**Aiding fast starts**

For Independent Power Producers to take advantage of short production intervals (one hour), it is important that compliance with environmental permits is met soon after ignition. The operating temperature window for DeNOₓ catalysts is 350 to 1,000°F, and the optimal temperature range is from 600 to 700°F. But simple cycle gas turbines operate typically between 800 and 1,150°F. At these higher temperatures it is more difficult to adsorb ammonia, and some catalysts will deactivate. Deactivation can be from sintering of the active sites or by deterioration due to thermal stress.

Catalysts in peaking units are exposed to extreme conditions because the ramp rates for simple cycle applications are typically many times higher than for other applications. For example, the LM6000s are typically at full load in 6 minutes with a ramp rate of 125°F/min. A catalyst with lower mass will be able to react faster to such changes in operating conditions. Also, if the porosity of the catalyst is high, a large number of active sites can be maintained with a lower catalyst mass and a correspondingly lower heat capacity. Further, if the pore size distribution has a large fraction of macro pores (larger than 10 μm), the temperature at the catalyst-active sites will depend primarily on the diffusion of heat to the surface, and consequently the catalytic reaction temperature will be reached almost instantaneously. This catalyst design enables NOₓ conversion within a few minutes of turbine ignition (Figure 4).

A major challenge with cyclic operation is to have reliable NOₓ readings in the short operating periods. It may take 15 minutes to calibrate the analyzer but if operators do not calibrate them run the risk of the plant being out of compliance for the full operating period due to a faulty analyzer. In a few cases, permits may allow a “grace calibration period” of 15-30 minutes.

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**Operating two catalysts**

More and more combustion turbines are being permitted with both CO oxidation and SCR catalysts. This has caused a problem for several plants that have discovered that the CO catalyst forms NO₂ as a result of oxidation of NO. At lower temperatures, the NO₂ can actually be beneficial to the SCR reaction:

NO + NO₂ + 2 NH₃ → 2 N₂ + 3 H₂O.

For NO₂/NOₓ ratios lower than 0.5, the NO₂ will enhance conversion by contributing to the re-oxidation of vanadium in the catalyst reaction cycle. At lower temperatures, vanadium re-oxidation is a limiting factor, whereas at higher temperatures ammonia adsorption on vanadia sites becomes the limiting step. And the NO₂ can be quite difficult to convert to N₂ at higher temperatures. Problems have been experienced in turbines where NO₂ fractions were as high as 70% of the total NOₓ. These can be solved by increasing catalyst volume to decrease the space velocity in the catalyst. [7]

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**Footnotes**

[1] For oil firing, Haldor Topsoe designs the SCR catalyst with an initial vanadium level so that SO₂ oxidation will remain within acceptable limits while meeting NOₓ levels.

[2] In two LM6000s that operated in simple cycle mode with Haldor Topsoe SCR catalyst the SCR showed a deactivation of 10% during the first 1,200 hours of operation (two calendar years) on a combination of oil and gas.

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**Authors**

Flemming Hansen is manager of SCR/DeNOₓ at Haldor Topsoe, Inc. He has 20 years of experience working with catalysts in utilities, ammonia manufacture and petrochemical industries. Reach him at fgh@topsoe.com

Peter Lindenhoff is the technical manager of DeNOₓ Haldor Topsoe, Inc. Before joining Haldor Topsoe in 1999, he worked as a process engineer for a Danish refinery and a Danish utility. He has over 15 years of experience with DeNOₓ systems.
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- high resistance to erosion
- high NOx conversion
- high poison resistance
- low SO₂ oxidation

Topsoe has supplied more than 400 SCR installations.